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Part I. The Onset of Detonation in the Sensitiveness of Explosives

A. R. Ubbelohde

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THE SENSITIVENESS OF EXPLOSIVES

By J. L. COPP, S. E. NAPIER, T. NASH, W. J. POWELL,
H. SKELLY, A. R. UBBELOHDE and P. WOODWARD

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PART I

THE ONSET OF DETONATION IN THE SENSITIVENESS OF EXPLOSIVES

By A. R. Ubbelohde

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Introduction

The ease with which explosives detonate on receiving a sharp blow or shock is of practical importance in determining manufacturing precautions and safety in handling, and also in deciding what initiators can be used. Physical tests on sensitiveness have hitherto imitated either manufacturing or service conditions as closely as possible. With any one physical test, such as that of the impact machine (cf. part III (1)), it is possible to arrange explosives in a scale of sensitiveness. The order of sensitiveness in a scale determined in any one way may be quite different from the order determined in other ways, but owing to the empirical nature of the tests it is often difficult to explain why anomalies occur. Results in accordance with each other are, however, obtained in many cases.

Progress in synthetic organic chemistry has increased the range of possible explosives to such an extent that some more scientific information on sensitiveness would be most useful in orienting future developments. Various developments in the experimental knowledge on the subject are discussed in the following sections.

The mechanism of initiation of detonation

In discussing the initiation of detonation in a quiescent explosive it is desirable to keep in view certain facts about the mechanism of propagation, once detonation has been started. The linear velocity of propagation in solids and liquids ranges from 3000 to 8000 m./sec., so that the front of the chemical reaction traverses a layer of quiescent molecules—say 3 Angstrom units—in not more than 10^{-13} sec. At ordinary temperatures, the frequency of molecular collision in a liquid is only about 3×10^{11} per sec. (Moelwyn-Hughes 1933). During the time the front of the detonation has advanced the distance of one layer of molecules, these molecules will not have performed more than 3×10^{-2} collisions amongst themselves. It is highly unlikely that this layer of molecules will have time to be activated by collisions amongst themselves, even though the temperature of the layer is rising by conduction and radiation from the gases behind the detonation front.

In view of the brief time available for chemical reaction, the most plausible mechanism for the propagation of detonation seems to be that collisions with molecules behind the detonation front activate those in the quiescent layer ahead. Practically every such collision must lead to activation. This unusually high activation efficiency of collisions is due to two factors:

(*a*) The molecules behind the detonation front have high *random* velocities on account of the high temperature.

(*b*) In addition, the molecules behind the detonation front are projected towards the unreacted layer with a high *directed* velocity, which results from the hydrodynamical conditions of propagation of a shock wave.

The extent to which 'physical' methods of initiation involve factors (*a*) and (*b*) varies from case to case. 'Sympathetic explosion' of one charge by another some distance away probably involves mainly the directed velocity factor (*b*) of the shock wave, whereas hot spots (cf. part III (1)) in mechanical processes may involve chiefly factor (*a*). The disentanglement of these factors in various sensitivity tests would be of definite value; various attempts are discussed in what follows.

The phenomenon, that as the density of packing an explosive is increased, more power is required to initiate detonation (cf. part II (2)), can be understood in the light of the fact that local activation will not lead to detonation unless a wave front can be built up to satisfy the hydrodynamic conditions of propagation. As the density increases, the increase in co-volume requires higher pressures and temperatures for stable propagation of a detonation wave.

Critical conditions for the propagation of detonation

Explosives differ markedly in the distance over which chemical reaction must travel before a stable wave is set up. The slow 'pick up' of T.N.T. may be adduced as an example. Again, explosives are phlegmatized by breaking up local concentrations to colloidal dimensions (cf. part III (1)). It seems likely that more information on this important aspect of sensitiveness is to be obtained from experiments on liquid explosives, since with liquids, diluents can be added which will mix on the molecular scale. The sensitiveness of liquid explosives may be expected to be closely related to the 'pick up' interval between initiation and stable detonation. Little work has, however, been published on liquids to date (1940) [see, however, Mulcahy & Yoffe (1945); Roth (1941)].

Special activation processes in solid explosives

In addition to the aspects of sensitiveness which can best be obtained from a study of liquid explosives, the solid state presents a number of fresh problems. One example is the effect of shearing stresses, which may break the crystals and initiate detonation (Carl 1940). Two comments may be made:

(*a*) In cases where shearing stress, leading to breaking of the crystals, can initiate detonation, the probability of occurrence will diminish with decreasing size of crystals. This is due to the fact that a crystal will break through shear only if this exceeds the holding strength of any crystal flaws. With small crystals the chance of slipping over one another will be increased, and a breakage of a single crystal will be less likely.

A sure sign that shear sensitiveness is important is that the addition of lubricants has a beneficial effect, e.g. with cheddites (chlorate mixtures) and with cyclonite.

(*b*) In addition to the breaking strength under shearing stresses, the lattice energy of the solid explosive will be of decisive importance.

The lattice energy may be defined as the total heat required to convert the crystal to a gas. It seems unlikely that any mechanical strains can give an additional activation energy to local spots in the crystal, exceeding this lattice energy. Thus when the lattice energy is high, sensitiveness to shear may be expected, but not when it is low.

Explosives which are salts, such as potassium perchlorate, the fulminates, and the azides, will have lattice energies ranging between 120 to 200 kcal./mol. A breaking of the crystal can obviously activate molecules in the freshly broken surfaces to an extent comparable with the activation energy required for initiating detonation, which, in the case of lead azide, is of the order of 40 kcal./mol. (see, however, part III (2)).

Organic compounds with high melting points, such as cyclonite, will have lattice energies which may be estimated to lie between 30 to 50 kcal./mol. Shear phenomena can still be of importance. Finally, compounds such as T.N.T. can be estimated to have such low lattice energies that any activation on breaking the crystal will be quite insufficient to initiate detonation.

Sensitiveness to friction in current tests probably involves a combination of local heating, and breaking of the crystals. A separation of these effects seems highly desirable.

Finally, with certain solids the possibility of building up electrical charges by friction, followed by a discharge through the crystals, may have to be considered amongst the causes of initiation of detonation. Electrical tests on the sensitiveness of explosives are discussed elsewhere.

Conclusions from the experimental work (1946)

Two main problems in the sensitiveness of explosives are the various ways in which chemical change is initiated—the 'trigger-actions'—and the ways in which such chemical change builds up into detonation. For utilitarian reasons the investigations described included the examination of certain routine tests on the sensitiveness of explosives to heat, percussion, and friction, and the redesign of these tests so as to give more definite physico-chemical information about sensitiveness. Amongst other investigations, an important process which was studied in various ways is the mode of build-up of detonation when a powdered initiator is heated. It has been verified that an activation energy characteristic of the initiator controls the onset of detonation, which takes place after an induction period (part II (1), (2) and (3)). During this induction period, physico-chemical changes can be observed in the initiator; if the initiator is suddenly cooled before the end of the induction period, these changes persist, and the substance is permanently sensitized to heat. Permanent sensitization to heat can also be produced by exposure of initiators such as lead azide to light (part II (1)).

The onset of detonation, i.e. the formation of a detonation wave which passes through the whole mass of initiator, is critically controlled by other factors, as well as the activation energy. The total mass of initiator (when this is small) (part II (1), (2) and (3)) and the bulk-density (part II (2)) can determine whether the processes occurring during the induction period build up into detonation, or merely fade out after a time. This fading-out has been related to the phenomenon of 'dead-pressing' of initiators. Dilution of one initiator by another with a different activation energy, or by inert powder, and replacement of the air normally present between the grains of initiator, by various liquids and vapours, has also been used to investigate the mechanism of 'build-up' (parts I (1) and II (3)). Particularly interesting differences of behaviour are exhibited by lead azide in the form of small single crystals, and in the form of polycrystalline nodules with very much smaller crystallites (dextrinated azide) (part II (1)).

The main outcome of these investigations on the sensitiveness to heat has been to support a theory of build-up of detonation in initiators, by a process conveniently described as 'mass-flow', which differs from the build-up in high explosives, by a process of 'self-heating' (parts II (2) and III (1)). As outlined above, and as discussed more fully in subsequent pages, the energy liberated in the decomposition of an explosive can be much more efficiently utilized for activation of neighbouring portions of explosive, in a process such as 'mass-flow', than in 'self-heating'. In consequence, quite small masses of initiator in which self-heating is almost negligible can give rise to detonation. But with larger masses, the two processes may be competitive under certain conditions, and have been observed side by side (part II (3)).

When various 'mechanical' tests on sensitiveness are examined, such as the sensitiveness to percussion and to friction (parts III (1), (2) and IV (1)) the problem arises in each case whether the mechanical processes in the explosive merely lead to the local generation of heat, which if sufficiently intense will give rise to detonation of the main mass, by mechanisms similar to those observed under conditions of uniform heating, or whether the mechanical energy can be more economically transformed into activation energy, e.g. by the stretching and breaking of valency bonds, than would be the case if the mechanical energy were first transformed into heat.

An outstanding example in which mere heating appears to be sufficient to account for the effects, is the grit-sensitiveness of explosives (part III (1)). In view of its practical as well as its theoretical importance, fairly extensive investigations were made on the grit-sensitiveness both of high explosives and of initiators. A theory was advanced for the production of a 'hot-spot' round each particle of grit, when the explosive is subjected to mechanical action. These hot-spots can grow into explosion as a result of the heat liberated by the (exothermic) chemical decomposition of the explosive. Evidence was obtained that the mode of action of phlegmatizers when added to explosives is to damp down the development or growth of such hot spots, rather than to prevent their formation.

Although grit-sensitiveness appears to be simply explained in terms of local heating around the particles of grit, in various other mechanical tests on sensitiveness there does appear to be some evidence of 'tribo-chemical' activation, defined as a *transfer of mechanical into activation energy, without prior Maxwellian degradation into heat*. Particularly in the case of initiators, the order of sensitiveness in various mechanical tests, and the behaviour of initiators partly sensitized to heat, suggests that 'trigger-actions' other than the formation of local hot-spots may contribute to the sensitiveness. A notable fact is that the temperature coefficient of sensitiveness, e.g. to friction, is very small (part III (2)).

Co-operative build-up of detonation

The following theory of co-operative build-up of detonation by mass-flow was put forward in a report first issued by the Armaments Research Department on 26 November 1943. The essential feature is to provide a mechanism of critical change-over from local thermal decomposition, controlled by thermal activation, to hydrodynamic activation in a detonation wave. It is postulated that detonation can occur by co-operative decomposition of adjoining crystals as well as by simultaneous activation of several atoms in the same crystal, as proposed by Garner & Gomm (1931) and Muraour (1934).

Theory of heat sensitiveness of initiators

The hypothesis suggested on the basis of previous experimental results (part II (1)) was that when individual crystals of initiator are too small to detonate alone, pressure pulses around these individual crystals may build up a pressure wave in the surrounding gas, rather like Huyghens wavelets building into a light wave. The integrated pressure wave will however only pass into stable detonation if it is sufficiently intense to activate the decomposition of adjacent grains by sympathetic detonation.

Four properties of an initiator are involved in this building-up process:

(i) The rate of decomposition round individual crystals or grains, forming pressure 'wavelets'.

(ii) The effective bulk density of the grains under the conditions envisaged, which determines the intensity of the pressure wave.

(iii) The threshold intensity of the integrated pressure wave, which will suffice to initiate adjacent layers by sympathetic detonation.

(iv) Once stable detonation is built up, an initiator like lead azide may lead to more intense detonation than say mercury fulminate.

The way these different factors affect the pick up can be illustrated in terms of a very much simplified picture, as follows:

Consider a layer of grains of initiator, undergoing decomposition under conditions such that 'self-heating' due to inadequate conduction of heat can be neglected. Individual grains are assumed to be considerably smaller than the smallest crystal which can detonate alone, as appears to be the case for the polycrystalline masses which make up 'Service' initiators.

If there are n grains per unit area of layer, and each grain is evolving x mol. of gas/sec., the number of gram molecules liberated per unit area is nx mol./sec. The intensity of the pressure wave built up in the surrounding gas will depend on the rate of release of this gas into free air. To obtain some limiting idea of the intensity of shock wave set up by the layer of decomposing explosive, the flow nx mol./sec./unit area may be considered as equivalent to the mass motion immediately behind the front of a shock wave.

According to standard theory, the velocity D of the shock wave is related to the pressure difference (p_2-p_1) at the front, by the equation

$$DW = (p_2-p_1)/d_1,$$

where W is the velocity of the particles streaming towards the undisturbed gas in front of the wave and d_1 is the density of the undisturbed gas before it is reached by the pressure pulse. The number of molecules streaming towards the undisturbed gas will be, per unit area per sec., if M is the molecular weight,

$$Wd_2/M = nx,$$

where d_2 is the density of gas immediately behind the shock wave, i.e. the critical condition for detonation under these conditions is

$$(p_2-p_1)\, d_2/D\,.\,d_1 = Wd_2 = Mnx.$$

This equation relates the velocity of decomposition of the grains, with the properties of the resulting shock wave built up in the surrounding gas. When the intensity of this wave reaches a sufficient magnitude or threshold, it is assumed that the whole mass of initiator will undergo sympathetic detonation.

Attention is drawn to the following points:

(*a*) The intensity of the wave built up from products of thermal decomposition will be greater the greater the packing density of grains (as determined by n) and also the greater the rate of thermal decomposition (determined by x) and the molecular weight M of the gaseous reaction products.

(*b*) The properties of the initial wave built up depend on the nature of the surrounding gas, e.g. mercury fulminate might be expected to show different induction periods according as it is surrounded by air or CO_2, unless its decomposition products displace the surrounding gas before detonation occurs (cf. part II (3)).

(*c*) The mechanism of build-up should not apply in a maintained vacuum, though this effect may be masked if gases can accumulate from the decomposition of the initiator.

In comparing this theory with experiment, the following lines of evidence are available.

(1) *Threshold intensity of shock wave.* This might, in principle, be measured, e.g. in the gap test, for different initiators.

The effect of *hot spots of various temperatures* T_1 on the attainment of the threshold, in various initiators, can be allowed for by assuming a rate of decomposition per grain of the general form

$$x = Ae^{-E/RT_1}.$$

Then

$$nMx = nA'e^{-E/RT_1}$$

giving

$$nA'e^{-E/RT_1} = \frac{(p_2-p_1)\,d_2}{D\,.\,d_1} \quad \text{(where } A' = \text{constant} = MA\text{)}.$$

Thus mechanisms of sensitiveness involving high temperatures at local spots would tend to make initiators with high activation energy appear relatively more sensitive.

For the present purpose the mechanism whereby a shock wave sets off the initiator need not be specified in detail, except that as discussed above, non-random molecular collisions are operative in the activation process.

(2) The effect of decreasing crystal size is to increase n, and is likely to have a noticeable effect in diminishing the quantity of initiator required for stable build-up.

(3) The induction period to ignition is likely to be affected by the nature of *the surrounding gas*. The known effect of a vacuum in inhibiting the detonation of small quantities of mercury fulminate is in accordance with this theory.

(4) Once the adjacent layers have been brought to detonation, the initiation of other layers becomes a property of the stable detonation wave, whose compression ratio and velocity are determined by the density and temperature of the explosion products of the initiator, not of the surrounding gas. This accounts for the fact that although mercury fulminate may be more easily initiated than lead azide, the *stable* wave in fulminate may not lead to as rapid a pressure rise in other explosives placed in contact, as in the case of lead azide.

(5) If conditions in the heat test are such that the critical intensity of shock wave does not build up, the initiator will merely decompose thermally and show a 'failure' (parts II (1), (2) and (3)).

Although this simplified picture of co-operative initiation of detonation may require modification as more information becomes available, it forms a useful basis for further experimental work on initiators.